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THE CRYSTAL CHEMISTRY OF SHCHERBAKOVITE FROM THE KHIBINA MASSIF, KOLA PENINSULA, RUSSIA

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ABSTRACT

The crystal structure of shcherbakovite from Mount Rasvumchorr, Khibina massif, Kola Peninsula, Russia, ideally K_2 Na Ti^{4+}_2 O (OH) [Si_4O_{12}], *a* 8.1538(4), *b* 10.5569(5), *c* 13.9882(6) Å, *V* 1204.1(2) Å^3, space group *Imma*, *Z* = 4, D_{calc} 3.194 g/cm^3, has been refined to R_1 = 3.2% for 960 unique ($F_o > 4\sigma F$) reflections collected on a Bruker single-crystal *P*4 diffractometer equipped with a CCD detector and Mo*K*α X-radiation. Shcherbakovite occurs in late (hydrothermal) shallowly dipping veins of natrolite and is associated with natrolite, aegirine, K-feldspar, strontian apatite, titanite, spherulitic baryllite and rare pyrrhotite and chalcopyrite. Electron-microprobe analysis gave SiO_2 40.57, TiO_2 18.87, Fe_2O_3 1.05, MnO 0.06, BaO 6.7, CaO 0.20, K_2O 13.22, Na_2O 5.59, Nb_2O_5 10.49, SrO 0.08, ZrO_2 0.84, Ta_2O_5 0.06, $(H_2O)_{calc}$ 0.73, sum 97.83 wt.%. The amount of H_2O was determined from crystal-structure analysis. There is one tetrahedrally coordinated *T* site, <*T*–O> 1.607 Å, occupied by Si. There are two octahedrally coordinated sites, *M*(1), occupied by ($Ti_{0.68}$ $Nb_{0.32}$ $\square_{1.00}$), with <*M*(1)–O> = 2.016 Å, and *M*(2), occupied by ($Ti_{0.72}$ $Nb_{0.15}$ $Fe^{3+}_{0.08}$ $Zr_{0.04}$ $\square_{1.01}$), with <*M*(2)–O> = 1.999 Å. The *M*(1) and *M*(2) sites are separated by 0.477 Å, and hence cannot be occupied simultaneously at a local level. There are three interstitial *A* sites: the *A*(1) site is [9]-coordinated and is occupied by ($K_{0.66}$ $Ba_{0.23}$ $Na_{0.07}$ $Ca_{0.02}$), with <*A*(1)–O> = 2.952 Å; the *A*(2) site is [8]-coordinated and is occupied by K, with <*A*(2)–O> = 2.861 Å, and the *A*(3) site is [6]-coordinated and is occupied by Na, with <*A*(3)–O> = 2.493 Å. Shcherbakovite is a K-analogue of batisite, ideally Ba Na_2 Ti^{4+}_2 O_2 [Si_4O_{12}]. Shcherbakovite is related to batisite by substitution of K for Ba and K for Na. "Noonkanbahite", ideally Ba K Na Ti^{4+}_2 O_2 [Si_4O_{12}], has never been approved by the IMA as a new mineral species. Based on the crystal chemistry of this structure type, the general formula of these minerals may be written as $A\ B\ C\ M_2\ \phi_2$ [Si_4O_{12}], with the following end-member compositions: batisite *A* = Ba, *B* = Na, *C* = Na; shcherbakovite, *A* = K, *B* = K, *C* = Na; "noonkanbahite", *A* = Ba, *B* = K, *C* = Na; unnamed, *A* = K, *B* = Na, *C* = Na.

Keywords: shcherbakovite, batisite, end-member, crystal-structure refinement.

SOMMAIRE

Nous avons affiné la structure cristalline de la shcherbakovite provenant du mont Rasvumchorr, complexe alcalin de Khibina, péninsule de Kola, en Russie, dont la composition idéale est K_2 Na Ti^{4+}_2 O (OH) [Si_4O_{12}], *a* 8.1538(4), *b* 10.5569(5), *c* 13.9882(6) Å, *V* 1204.1(2) Å^3, groupe spatial *Imma*, *Z* = 4, D_{calc} 3.194 g/cm^3, jusqu'à un résidu R_1 = 3.2% pour 960 réflexions uniques ($F_o > 4\sigma F$) prélevées sur monocristal avec un diffractomètre Bruker *P*4 muni d'un détecteur CCD (rayonnement Mo*K*α). On trouve la shcherbakovite dans des veins hydrothermales tardives de natrolite à faible pendage, en association avec natrolite, aegyrine, feldspath potassique, apatite strontifère, titanite, baryllite sphérulitique, et, plus rarement, pyrrhotite et chalcopyrite. Les analyses à la microsonde électronique ont donné SiO_2 40.57, TiO_2 18.87, Fe_2O_3 1.05, MnO 0.06, BaO 6.7, CaO 0.20, K_2O 13.22, Na_2O 5.59, Nb_2O_5 10.49, SrO 0.08, ZrO_2 0.84, Ta_2O_5 0.06, $(H_2O)_{calc}$ 0.73, somme 97.83% (poids). La quantité de H_2O a été déterminée par ébauche de la structure cristalline. Il y a un site à coordinence tétraédrique *T*, <*T*–O> 1.607 Å, qu'occupe le Si. Il y a deux sites à coordinence octaédrique, *M*(1), qu'occupe ($Ti_{0.68}$ $Nb_{0.32}$ $\square_{1.00}$), avec <*M*(1)–O> = 2.016 Å, et *M*(2), qu'occupe ($Ti_{0.72}$ $Nb_{0.15}$ $Fe^{3+}_{0.08}$ $Zr_{0.04}$ $\square_{1.01}$), avec <*M*(2)–O> = 1.999 Å. Les sites *M*(1) et *M*(2) sont 0.477 Å l'un de l'autre, et donc ne pourraient pas être remplis simultanément à un échelle locale. Il y a trois sites interstitiels *A*: Le site *A*(1) possède une coordinence [9] et contient ($K_{0.66}$ $Ba_{0.23}$ $Na_{0.07}$ $Ca_{0.02}$), avec <*A*(1)–O> = 2.952 Å; le site *A*(2) possède une coordinence [8], et contient le K, avec <*A*(2)–O> = 2.861 Å, tandis que le site *A*(3) a une coordinence [6], et contient le Na, avec <*A*(3)–O> = 2.493 Å. La shcherbakovite est l'analogue à dominance de K de la batisite, dont la formule idéale est Ba Na_2 Ti^{4+}_2 O_2 [Si_4O_{12}]. Dans la shcherbakovite, il y a remplacement du Ba et du Na par le K. La "noonkanbahite", dont la formule idéale serait Ba K Na Ti^{4+}_2 O_2 [Si_4O_{12}], n'a pas été

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acceptée par l'IMA comme nouvelle espèce minérale. Selon la cristallochimie de ce type de structure, la formule générale de ces minéraux serait $A\ B\ C\ M_2\ \phi_2\ [Si_4O_{12}]$, avec les pôles suivants: batisite, A = Ba, B = Na, C = Na; shcherbakovite, A = K, B = K, C = Na; "noonkanbahite", A = Ba, B = K, C = Na; espèce sans nom, A = K, B = Na, C = Na.

(Traduit par la Rédaction)

Mots-clés: shcherbakovite, batisite, pôle, affinement de la structure cristalline.

INTRODUCTION

Shcherbakovite, ideally $K_2\ Na\ Ti_2\ O\ (OH)\ [Si_4O_{12}]$, was first discovered in an agpaitic pegmatite vein in the Khibina massif, Kola Peninsula, and was described as a new mineral by Es'kova & Kazakova (1954). The holotype occurrence of the mineral is confined to a pectolite–natrolite vein cutting leucite-normative kalsilite–nepheline rischorrite at Mount Rasvumchorr. These rocks differ from other poikilitic syenites of the Khibina complex in having high K_2O contents (8.21 to 15.4 wt.%), molar K/Na ratios of up to 2.6, and by the presence of leucite, kalsilite and wadeite in their normative composition (Arzamastsev 1994). Shcherbakovite commonly occurs in pegmatites and zeolite-bearing hydrothermal veins within both the hanging-wall rocks at the Rasvumchorr deposit and within the "Central Plug" of the Khibina complex (Khomyakov 1995), in which the semicircular rischorrite zone is one of the major constituents.

The Ba–Na analogue of shcherbakovite, batisite, was subsequently recognized as a rock-forming mineral in peralkaline rocks of the Inagli complex, Aldan, Siberia; Kravchenko *et al.* (1960) reported that batisite, $(Ba,Ca,Mn,Sr)_{\Sigma 0.92}\ K\ Na\ (Ti_{1.68}\ Fe_{0.14}\ Zr_{0.09}\ Al_{0.11})_{\Sigma 2.02}$ $(O_{1.66}(OH)_{0.34})_{\Sigma 2.00}\ [Si_4\ O_{12}]$, and shcherbakovite form a solid-solution series with the following isomorphic scheme: $Ba + Ti^{4+} \leftrightarrow K(Na) + Nb$. However, we note that neither batisite nor shcherbakovite contain essential Nb, and hence this scheme cannot be correct. Nikitin & Belov (1962) solved the crystal structure of batisite. On the basis of a piezoelectric effect, they chose the space group *Ima*2, a 10.40, b 13.85, c 8.10 Å, V 1166.7 Å^3, Z = 4. Yakovlevskaya & Efimov (1963) provided additional crystallographic data on the shcherbakovite–batisite series. Prider (1965) described a K–Ba–Ti silicate, $(Ba_{0.55}\ K_{0.20}\ Ca_{0.18})_{\Sigma 0.93}\ K\ (Na_{0.84}\ K_{0.16})_{\Sigma 1.00}\ (Ti_{1.55}\ Fe_{0.18}\ Zr_{0.01}\ Al_{0.01}\ Si_{0.21})_{\Sigma 1.99}\ (O_{1.39}\ (OH)_{0.61})_{\Sigma 2.00}\ [Si_4\ O_{12}]$, under the name "noonkanbahite", but it was not approved by the IMA. Schmahl & Tillmanns (1987) refined the crystal structure of batisite, $(Ba_{0.60}\ K_{0.40})\ (K_{0.70}\ Na_{0.30})\ Na\ (Ti_{1.72}\ Fe_{0.16}\ Nb_{0.06}\ Zr_{0.06})_{\Sigma 2.00}\ O_2\ [Si_4\ O_{12}]$, from Tertiary nephelinite–leucite volcanic rocks from Westeifel, Germany. There was no second harmonic-generation response for a single crystal, and they used the space group *Imam*; attempts to refine the structure in *Ima*2 were unsuccessful (Schmahl & Tillmanns 1987). On the other hand, Rastsvetaeva *et al.* (1997) refined K-rich batisite in the space group *Ima*2.

Currently, minerals of the shcherbakovite–batisite series have been described from a range of (K,Na)-rich to ultrapotassic silica-undersaturated rocks considered to be of mantle origin. Shcherbakovite–batisite minerals of intermediate composition have been described from pneumatolitic parageneses lining vesicles in Si-rich lamproites of the Leucite Hills, Wyoming (Mitchell 1990), as inclusions in "sanidine derived from leucite" in a lamproite dyke in Baffin Island, Canada (Hogarth 1997), and as a mineral common in lamproite pegmatites at the Walgidee Hills, western Kimberley, Australia (Prider 1965). Crystallization of shcherbakovite in a low-temperature zeolite paragenesis at Khibina indicates that a very wide P–T range of stability can be expected for the members of the group. The structure of these minerals is tolerant to a wide range of isomorphic substitutions at the cation sites. This structural flexibility allows shcherbakovite–batisite to be a sink for high field-strength and large-ion lithophile elements in parageneses ranging from mantle conditions to postmagmatic evolution of peralkaline rocks in the upper lithosphere.

Here, we report on the crystal structure of shcherbakovite from Mount Rasvumchorr, Khibina massif, Kola Peninsula, Russia and the crystal chemistry of the batisite–shcherbakovite group.

OCCURRENCE AND MINERAL ASSOCIATION

Shcherbakovite has been found at the northwestern ridge of Mount Rasvumchorr, in shallowly dipping hydrothermal veins of semitransparent columnar natrolite. The veins vary from 3 to 20 cm in thickness and cut poikilitic syenites, described by Kozyreva *et al.* (1990) as a kalsilite–nepheline-bearing ultrapotassic variety of rischorrite. The veins have selvages 3–5 cm wide composed of green acicular aegirine and yellow potassium feldspar. Shcherbakovite forms prismatic crystals ranging from a few mm to 6 cm in length (Fig. 1), embedded in natrolite. The paragenesis includes relatively large well-shaped single prisms of black aegirine–diopside, slightly corroded blocky orthoclase, euhedral 1–2 cm crystals of strontian fluorapatite (SrO 18.7–22.3, F up to 4.2 wt.%), anhedral colorless titanite (cores of grains contain up to 8.6 wt.% ZrO_2, 5.6 wt.% Nb_2O_5

and 1.1 wt.% Al_2O_3), and rare grains of pyrrhotite and chalcopyrite and laths of manganoan pectolite up to 20 cm in length, which in places have been completely replaced by a fine-grained mixture of Fe–Mn oxides.

The majority of the shcherbakovite-bearing veins were affected by faulting along their axial zones, and were injected by additional hydrothermal solutions, which resulted in deposition of spherulites of baryllite 1–5 mm in diameter and caused fragmentation of crystals and coating of large shcherbakovite crystals by an unidentified enamel-like yellowish silicate phase, in addition to the alteration of Mn-rich pectolite, titanite and apatite. The most homogeneous and transparent crystals of shcherbakovite occur on slightly corroded surfaces of K-feldspar. One representative crystal, 1.5 mm in length, was broken and a fragment was selected for single-crystal structure refinement.

X-RAY DATA COLLECTION AND STRUCTURE REFINEMENT

X-ray-diffraction data for shcherbakovite were collected with a Bruker *P*4 diffractometer equipped with a SMART 1K CCD detector (Mo*K*α radiation) from a single crystal of shcherbakovite with dimensions 0.30 × 0.08 × 0.08 mm. The intensities of 5645 reflections with $\overline{11} < h < 11$, $\overline{14} < k < 14$, $\overline{19} < l < 18$ were collected to 59.99° 2θ using 25 s per 0.125° frame: an empirical absorption-correction (SADABS, Sheldrick 1998) was applied. The refined unit-cell parameters were obtained from 1632 reflections with $I > 10\sigma I$. Using atom coordinates of batisite (Schmahl & Tillmanns 1987), the crystal structure of shcherbakovite was refined to $R_1 = 0.032$ and a Go*F* value of 1.325 for 986 independent reflections (76 refined parameters including extinction) with the Bruker SHELXTL version 5.1 system of programs.

In the course of the refinement, the *M* site was characterized by a high value of the displacement parameter along the *a* axis ($U_{11} = 0.09$). A difference-Fourier map revealed a maximum of 4.5 *e* located 0.51 Å from the *M* site. This maximum was included in the refinement as the *M*(2) site, and the initial *M* site was relabeled as *M*(1). Site occupancies were refined for the two *M* sites (occupied primarily by Ti and Nb) and three *A* sites (occupied primarily by K, Ba and Na).

Details of the data collection and structure refinement are given in Table 1, final atom-parameters are given in Table 2, selected interatomic distances and angles in Table 3, refined site-scattering values and assigned populations for selected sites are given in Table 4, and bond-valence values are given in Table 5. A structure-factor table may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

CHEMICAL COMPOSITION

After collecting the X-ray-diffraction data, the crystal of shcherbakovite was polished and analyzed with a Cameca SX 100 electron microprobe operating in wavelength-dispersion mode with an accelerating voltage of

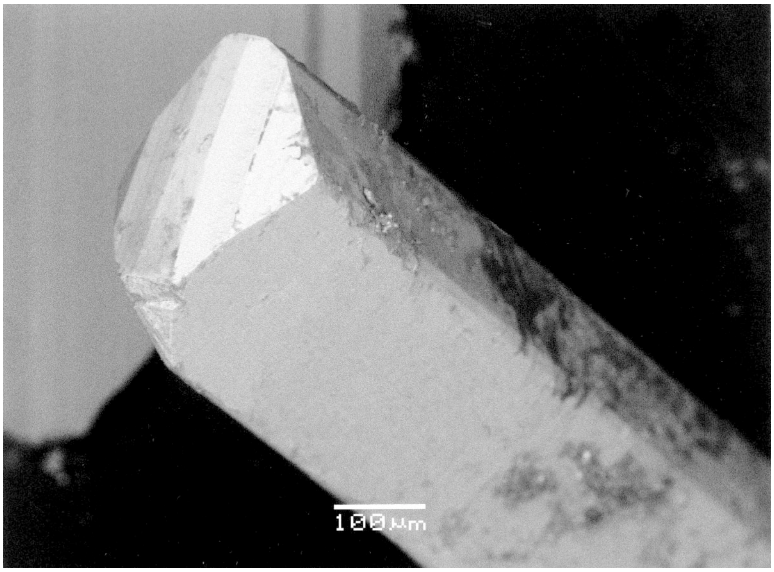

FIG. 1. Secondary electron image of shcherbakovite crystal.

15 kV, a specimen current of 20 nA, a beam size of 20 μm and count times on peak and background of 20 and 10 s, respectively. The following standards and crystals were used for *K, L* or *M* X-ray lines: Na: albite, Si, Ca: diopside, Mg, Al: spinel, K: orthoclase, Ti: titanite, Ba: barite, Mn: spessartine, Nb: $LiNbO_3$, Sr: $SrTiO_3$, Zr: zircon, Fe: fayalite, and Ta: manganotantalite. Data were reduced using the ϕ(ρz) procedure (Merlet 1992). The amount of H_2O was calculated from the structure refinement. Table 6 gives the chemical composition and empirical formula unit based on 14 anions including 0.48 OH groups *pfu* (per formula unit): $(K_{0.66}\ Ba_{0.23}\ Na_{0.07}\ Ca_{0.02})_{\Sigma 0.98}\ K_{1.00}\ Na_{1.00}\ (Ti_{1.40}\ Nb_{0.47}\ Fe_{0.08}\ Zr_{0.04})_{\Sigma 1.99}\ (O_{1.52}\ OH_{0.48})_{\Sigma 2.00}\ [Si_4\ O_{12}]$.

TABLE 1. MISCELLANEOUS REFINEMENT DATA FOR SHCHERBAKOVITE

a (Å)	8.1538(4)
b	10.5569(5)
c	13.9882(6)
V (Å^3)	1204.09(18)
Space group	*Imma*
Z	4
Absorption coefficient	3.41 mm^{-1}
F(000)	1117.0
$D_{calc.}$ (g/cm^3)	3.194
Crystal size (mm)	0.30 x 0.08 x 0.08
Radiation/ filter	MoKα/graphite
2θ-range for data collection (°)	59.99
R(int) (%)	2.39
Reflections collected	5645
Independent reflections	986
$F_o > 4\sigma F_o$	960
Refinement method	Full-matrix least squares on F^2, fixed weights proportional to $1/\sigma F^2$
Goodness of fit on F^2	1.325
Final $R_{(obs)}$ (%) $[F_o > 4\sigma F]$	*R*1 = 3.16
R indices (all data) (%)	*R*1 = 3.26 *wR*2 = 8.62 Goo*F* = 1.325

Description of the Structure

Cation sites

In the crystal structure of shcherbakovite, there is one *T* site occupied by Si with <Si–O> = 1.607 Å. There are two *M* sites, *M*(1) and *M*(2), partly occupied by Ti and Nb, with *M*(1)–*M*(2) = 0.477 Å, and hence only one of these two sites can be locally occupied. The *M*(1) site is occupied by $(Ti_{0.68}\ Nb_{0.32}\ \square_{1.00})$ with <*M*(1)–O> = 2.016 Å, and the *M*(2) site is occupied by $(Ti_{0.72}\ Nb_{0.15}\ Fe^{3+}_{0.08}\ Zr_{0.04}\ \square_{1.01})$ with <*M*(2)–O> = 1.999 Å. This splitting of the *M* site is in accord with the results of Schmahl & Tillmanns (1987). Although they reported only a single (non-split) *M* site, one of the displacement parameters is (on average) fifteen times larger than the other two displacement parameters for this site.

There are three interstitial *A* sites: the *A*(1) site is occupied by $(K_{0.66}\ Ba_{0.23}\ Na_{0.07}\ Ca_{0.02})$, the *A*(2) site is occupied by K, and the *A*(3) site is occupied by Na. In previous structural studies of batisite, the *A*(1), *A*(2) and *A*(3) sites are described as [12]-, [11]- and [10]-coordinated by Schmahl & Tillmanns (1987) and Rastsvetaeva *et al.* (1997), and [12]-, [11]- and [9]-coordinated by Nikitin & Belov (1962). For the coordination numbers [12], [11] and [10], the incident bond-valence sums at the *A*(1), *A*(2) and *A*(3) sites in shcherbakovite are 1.118, 1.129 and 1.142 valence units (*vu*), respectively, and the ideal values, derived from the site populations of Table 4, are 1.26, 1.00 and 1.00 *vu*. Examining the bond-valence sums around the anions (Table 5) indicates that the sum at the O(4) anion is somewhat high at 2.25 *vu*. There are several long *A*–O distances in shcherbakovite (Fig. 2); should these be considered as chemical bonds? Inspection of Table 5 indicates that there are five distances that involve bond valences in the range 0.034–0.050 *vu*. If we wish to discount any of these distances as bonds, we must discount all of these distances as bonds. If this is done, the corresponding incident bond-valence sums at *A*(1), *A*(2) and *A*(3) are 1.000, 1.004 and 0.998 *vu*, and the sum at the O(4) site is 2.14 *vu*.

TABLE 2. FINAL ATOM POSITIONS AND DISPLACEMENT PARAMETERS FOR SHCHERBAKOVITE

	x	*y*	*z*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
M(1)	0.278(1)	3/4	0.4721(1)	0.0100(6)	0.0155(17)	0.0072(4)	0.0074(4)	0	0.0005(5)	0
M(2)	0.220(2)	3/4	0.4692(2)	0.0152(10)	0.0288(29)	0.0089(5)	0.0080(5)	0	0.0008(8)	0
A(1)	0	1/4	0.74564(5)	0.0189(3)	0.0218(4)	0.0168(4)	0.0180(4)	0	0	0
A(2)	0	3/4	0.68880(9)	0.0227(3)	0.0195(5)	0.0184(5)	0.0303(6)	0	0	0
A(3)	0	1/2	1/2	0.0296(5)	0.0179(9)	0.0360(13)	0.0350(13)	−0.0220(11)	0	0
T	−0.30493(7)	0.97562(5)	0.64432(4)	0.0106(2)	0.0125(3)	0.0094(3)	0.0099(3)	−0.0003(2)	0.0003(2)	−0.00002(20)
O(1)	−0.2213(2)	0.8826(2)	0.5685(1)	0.0161(3)	0.0245(8)	0.0118(7)	0.0118(7)	−0.0027(6)	0.0024(6)	0.0012(6)
O(2)	−0.2511(2)	0.1204(2)	0.6317(1)	0.0200(4)	0.0367(10)	0.0104(8)	0.0128(8)	0.0005(6)	0.0011(7)	−0.0032(7)
O(3)	−1/4	0.92534(3)	3/4	0.0288(7)	0.0635(20)	0.0127(11)	0.0102(11)	0	−0.0051(11)	0
O(4)	−1/2	0.9622(4)	0.6439(4)	0.0525(12)	0.0114(12)	0.0468(22)	0.0993(36)	−0.0161(22)	0	0
O(5)	0	3/4	0.4600(3)	0.0189(7)	0.0235(17)	0.0176(16)	0.0157(16)	0	0	0
O(6)	1/2	3/4	0.4785(3)	0.0229(8)	0.0227(17)	0.0188(17)	0.0273(19)	0	0	0

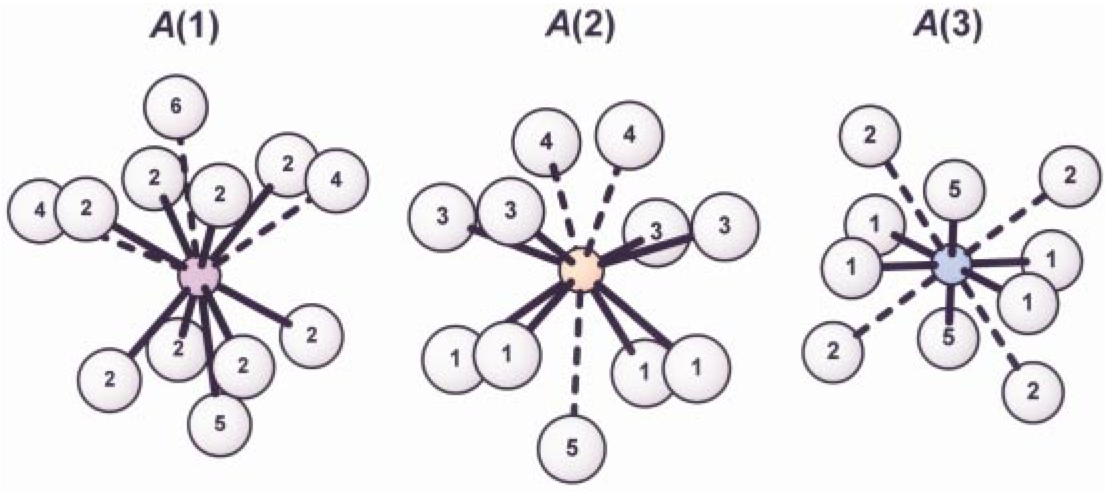

FIG. 2. The *A* sites and surrounding anions, showing relatively strong chemical bonds (black lines) and non-bonding contacts (dashed lines); the *A*(1), *A*(2) and *A*(3) sites are shown as mauve, orange and blue circles, respectively, and the O atoms are shown as grey circles.

These values indicate that the coordination numbers of the *A*(1), *A*(2) and *A*(3) sites are [9], [8] and [6], respectively, rather than [12], [11] and [10] or [9]. Similar calculations for batisite also indicate that the coordination numbers of the *A*(1), *A*(2) and *A*(3) sites are [9], [8] and [6].

Topology of the structure

In the structure of shcherbakovite, [SiO$_4$] tetrahedra link together to form an [Si$_4$O$_{12}$]$^{8-}$ chain first described in batisite (Nikitin & Belov 1962). This chain extends along the *a* axis (Fig. 2a), and (TiO$_6$) octahedra link *via* common vertices to form straight [TiO$_5$]$^{6-}$ chains extending along the *a* axis (Fig. 3a). These two types of chains, [Si$_4$O$_{12}$]$^{8-}$ and [TiO$_5$]$^{6-}$, link together to form a mixed tetrahedron–octahedron framework (Fig. 3b). Each [TiO$_6$] octahedron is connected through common vertices to four (SiO$_4$) tetrahedra, and each (SiO$_4$) tetrahedron is connected to two octahedra and two tetrahedra.

There are three types of interstitial cages (Fig. 3b), and they are significantly different in size. The largest cage includes the *A*(1) site and is populated by K, Ba, Na and minor Ca and Sr. The intermediate-sized cage

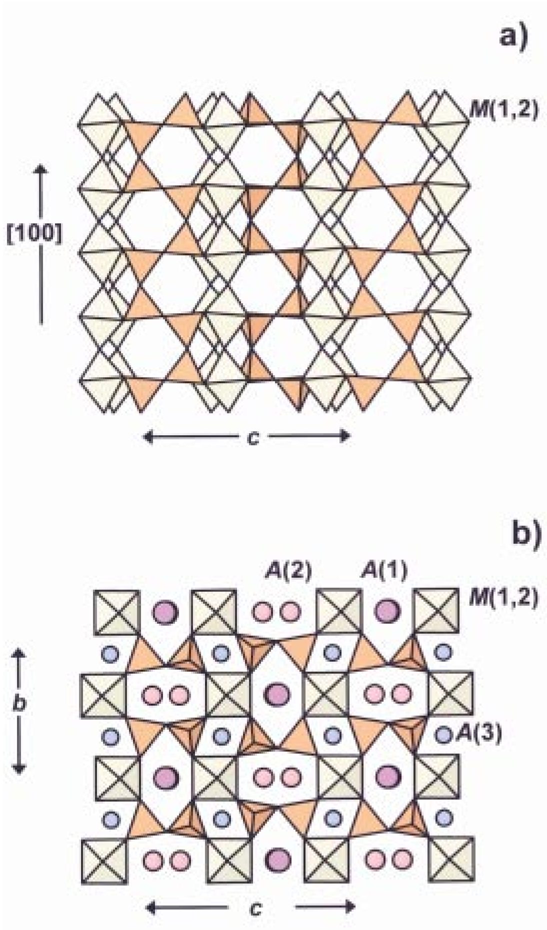

FIG. 3. The crystal structure of shcherbakovite: (a) a linkage of [Si$_4$O$_{12}$]$^{8-}$ chains and [TiO$_5$]$^{6-}$ perovskite-like chains; (b) viewed down [100]: (SiO$_4$) tetrahedra are orange, *M*(1,2) octahedra are honey yellow; *A*(1), *A*(2) and *A*(3) atoms are shown as mauve, orange and blue circles.

includes the *A*(2) site, and is occupied by K. The smallest cage includes the *A*(3) site and is occupied by Na.

The O(6) site

Calculation of the bond valence incident at O(6) in shcherbakovite gives 1.52 *vu* (Table 5). This calculation gives rise to two possibilities: (1) there is a symmetrical hydrogen bond *or* strong bi- or trifurcated hydrogen bonds, or (2) the O(6) site is partly occupied by $(OH)^-$ and O^{2-}. The site content of ($0.52\ O^{2-} + 0.48\ OH^-$) that is required for electroneutrality gives a value of $(H_2O)_{calc}$ of 0.73 wt.% (Table 6).

Splitting of the M site

We attempted to change the space group or origin (or both) of the structure to produce a single *M* site, but were unable to do so; hence we are forced to conclude that the splitting of the *M* site [to produce the *M*(1) and *M*(2) sites] is real. This splitting is presumably related to the occupancy of the O(6) site [and possibly the O(5) site] by both O^{2-} and $(OH)^-$. The local bond-valence situation for each case is shown in Figure 4. Where the bridging anion [O(br)] is O^{2-}, the *M*–O(br) bond-valences must be ~1.0 *vu*, whereas where the bridging anion is $(OH)^-$, the *M*–O(br) bond-valences must be ~0.5 *vu*; this arrangement may be modified slightly by the presence of the *A*(1)–O(5) bond, but we may ignore this (weak) bond for simplicity. As is apparent in Figure 4, O^{2-} and $(OH)^-$ anions will tend to alternate along the $[Ti^{4+}\phi_5]$ chain. So why does this pattern of order not produce a change in cell dimension or space group? Examination of Figure 3 shows that the $[Ti^{4+}\phi_5]$ chains do not link to each other; they are separated by silicate chains. Hence adjacent $[Ti^{4+}\phi_5]$ chains may adopt configurations with respect to O^{2-}–$(OH)^-$ order that are not coupled to each other. This random disorder results in an average structure in which the *M*–O^{2-} and *M*–$(OH)^-$ configurations overlap, with an apparent 50:50 splitting of the *M* site to produce the *M*(1) and *M*(2) sites observed here.

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR SHCHERBAKOVITE

T–O(1)		1.599(2)	*M*(1)–O(1)	x2	1.998(2)
T–O(2)		1.600(2)	*M*(1)–O(2)	x2	2.007(3)
T–O(3)		1.633(1)	*M*(1)–O(5)		2.275(8)
T–O(4)		1.597(1)	*M*(1)–O(6)		1.810(8)
<*T*–O>		1.607	<*M*(1)–O>		2.016
A(1)–O(2)	x4	2.933(2)	*M*(2)–O(1)	x2	1.971(2)
A(1)–O(2)a	x4	2.989(2)	*M*(2)–O(2)	x2	1.982(2)
A(1)–O(5)		2.876(4)	*M*(2)–O(5)		1.798(13)
<*A*(1)–O>		2.952	*M*(2)–O(6)		2.287(13)
			<*M*(2)–O>		1.999
A(1)–O(4)	x2	3.409(4)			
A(1)–O(6)		3.257(4)	*M*(1)–*M*(2)		0.477(2)
A(2)–O(1)	x4	2.837(2)			
A(2)–O(3)	x4	2.884(2)	*A*(3)–O(1)	x4	2.390(2)
<*A*(2)–O>		2.861	*A*(3)–O(5)	x2	2.698(2)
			<*A*(3)–O>		2.493
A(2)–O(4)	x2	3.239(5)			
A(2)–O(5)		3.201(4)	*A*(3)–O(2)	x4	3.034(2)

a: $x+1/2$, $-y+½$, $-z+3/2$

This splitting of the *M* site produces a complication in assigning the site populations, as at short range, where one of the sites is occupied, the locally associated site must be vacant. As noted above, the amount of splitting is controlled by the amount of O^{2-} and $(OH)^-$ at the bridging O(6) site, which is approximately 1:1 in this crystal. Thus the *M*(1) and *M*(2) sites will be each approximately half-occupied, which means that the dominant species at each site is a vacancy (Table 4). From a crystallographic perspective, which includes issues of short-range order, the *M*(1) and *M*(2) sites are distinct, whereas from the perspective of writing a chemical formula, the *M*(1) and *M*(2) sites need to be combined into one aggregate site that is then completely occupied (*cf.* Tables 4 and 6).

DISCUSSION

In Table 7, we summarize selected crystallographic data for the minerals of the shcherbakovite–batisite group. Structure refinements for batisite have been done in space groups *Ima*2 and *Imam*. In this work, we have used the space group *Imma* (standard setting). In Table 7, all formulae are given in a structurally appropriate fashion. *A*(1) is occupied by large cations K and Ba, *A*(2) is occupied solely by K or (K + Na), and *A*(3)

TABLE 4. REFINED SITE-SCATTERING VALUES (*epfu*) AND ASSIGNED SITE-POPULATIONS (*apfu*) FOR SHCHERBAKOVITE

	Refined site-scattering	Site population	Calculated site-scattering	$<X–\phi>_{calc.}$* (Å)	$<X–\phi>_{obs.}$ (Å)
A(1)	26.7(1.2)	0.66 K + 0.23 Ba + 0.07 Na + 0.02 Ca	26.6	2.957	3.053
M(1)	29.6(1.2)	0.68 Ti + 0.32 Nb + 1.00 □	28.1	1.996	2.016
M(2)	24.7(1.2)	0.72 Ti + 0.15 Nb + 0.08 Fe^{3+} + 0.04 Zr + 1.01 □	25.7	1.978	1.999

*Calculated by summing the constituent radii; values from Shannon (1976) is occupied solely by Na ($^{[9]}r_{Ba}$ = 1.47, $^{[9]}r_K$ = 1.55, $^{[8]}r_K$ = 1.51, $^{[6]}r_{Na}$ = 1.02 Å; Shannon 1976).

Using the criteria of Hawthorne (2002) for an end member, we can propose four end-members for the shcherbakovite–batisite solid-solution series:

Batisite	$Ba\ Na\ Na\ Ti_2\ O_2\ [Si_4O_{12}]$
Shcherbakovite	$K\ K\ Na\ Ti_2\ O(OH)\ [Si_4O_{12}]$
“Noonkanbahite”	$Ba\ K\ Na\ Ti_2\ O_2\ [Si_4O_{12}]$
Unnamed	$K\ Na\ Na\ Ti_2\ O(OH)\ [Si_4O_{12}]$

All formulae are neutral, they are compatible with the crystal structure of these minerals, their composition is fixed, and a maximum of one site contains two species in a fixed amount.

“Noonkanbahite” is not accepted as a valid mineral species, but according to our considerations, it should be regarded as such. Rastsvetaeva *et al.* (1997) investigated the crystal structure of K-containing batisite and gave the structural formula as $(Ba_{0.7}\ Ca_{0.1}\ \square_{0.2})\ K\ Na\ [Ti^{4+}\ (Ti^{4+}{}_{0.6}\ Fe^{3+}{}_{0.4})]\ (O,OH)_2\ [Si_4O_{12}]$; this formula corresponds to the chemical composition of “noonkanbahite”, ideally $Ba\ K\ Na\ Ti^{4+}{}_2\ O_2\ [Si_4O_{12}]$ (Prider 1965).

TABLE 5. BOND-VALENCE* TABLE FOR SHCHERBAKOVITE†

	A(1)**	*A*(2)**	*A*(3)*	*M*(1)*	*M*(2)*	*T* *	Σ
O(1)		$^{\times4}{\downarrow}0.135$	$^{\times4}{\downarrow}0.205$	$^{\times2}{\downarrow}0.356$	$^{\times2}{\downarrow}0.313$	1.063	2.07
O(2)	$^{\times4}{\downarrow}0.116$ $^{\times4}{\downarrow}0.100$		[$^{\times4}{\downarrow}0.036$]	$^{\times2}{\downarrow}0.348$	$^{\times2}{\downarrow}0.304$	1.060	1.93 [1.96]
O(3)		$^{\times4}{\downarrow}0.116^{\times2}{\rightarrow}$				$0.971^{\times2}{\rightarrow}$	2.17
O(4)	[$^{\times2}{\downarrow}0.034$]	[0.040]				$1.068^{\times2}{\rightarrow}$	2.14 [2.21]
O(5)	0.136	[0.045]	$^{\times2}{\downarrow}0.089^{\times2}{\rightarrow}$	$0.182^{\times2}{\rightarrow}$	$0.502^{\times2}{\rightarrow}$		1.68 [1.73]
O(6)	[$^{\times2}{\downarrow}0.050$]			$0.594^{\times2}{\rightarrow}$	$0.145^{\times2}{\rightarrow}$		1.48 [1.52]
Σ	1.000 [1.118]	1.004 [1.129]	0.998 [1.142]	2.184	1.881	4.162	

* bond-valence parameters (*vu*) from Brown (1981);
** bond-valence parameters (*vu*) from Brown & Altermatt (1985);
† values in [ ] calculated for *A*(1), *A*(2), *A*(3) coordination numbers [12], [11] and [10], respectively.

TABLE 6. CHEMICAL COMPOSITION* (wt.%) AND UNIT FORMULA (*apfu*) FOR SHCHERBAKOVITE

SiO_2	40.57	Si	3.99
TiO_2	18.87		
Fe_2O_3	1.05	Ti^{4+}	1.40
Nb_2O_5	10.49	Al	–
ZrO_2	0.84	Fe^{3+}	0.08
BaO	6.07	Nb	0.47
K_2O	13.22	Zr	0.04
CaO	0.20	Σ*M*	1.99
Na_2O	5.59		
H_2O**	0.73	Ba	0.23
Total	97.63	K	0.66
		Ca	0.02
		Na	0.07
		Σ*A*(1)	0.98
		K	1.00
		Σ*A*(2)	1.00
		Na	1.00
		Σ*A*(3)	1.00
		H	0.48

* Mn, Mg, Al, Ta, Sr, F, Cl not detected
** calculated from structural refinement

TABLE 7. CRYSTAL DATA FOR MINERALS WITH GENERAL FORMULA $A\ B\ C\ M_2\ (O,OH)_2\ [Si_4O_{12}]$

Mineral and Formulae	Space group	Unit cell parameters (Å)			<*A*–O> (Å)			Ref.
		a	*b*	*c*	(1)	(2)	(3)	
Shcherbakovite								
(1) $(K_{0.66}Ba_{0.23}Na_{0.07}Ca_{0.02}Sr_{0.01})_{0.99}K_{1.00}Na_{1.00}(Ti_{1.40}Nb_{0.47}Fe_{0.10}Zr_{0.04})_{2.01}(O_{1.52}(OH)_{0.48})[Si_4O_{12}]$	*Imma*	8.1538(4)	10.5569(5)	13.9882(6)	3.053	2.960	2.709	(1)
(2) $(K_{0.52}Ba_{0.24}Na_{0.09}Ca_{0.09}Mg_{0.04})_{0.98}K_{1.00}Na_{1.00}(Ti_{1.31}Nb_{0.46}Fe^{3+}{}_{0.13}Fe^{2+}{}_{0.04}Zr_{0.06})_{2.00}(O_{1.59}(OH)_{0.36}Cl_{0.05})$ $[(Si_{3.93}Al_{0.07})O_{12}]$								(2)
(3) $(K_{0.76}Ba_{0.24})(K_{0.76}Na_{0.10}Ca_{0.08}Zr_{0.05})Na_{1.00}(Ti_{1.31}Nb_{0.46}Fe^{3+}{}_{0.13}Fe^{2+}{}_{0.04}Mg_{0.04}Al_{0.03})(O_{1.60}OH_{0.35}Cl_{0.05})$ $[(Si_{3.94}Al_{0.06})O_{12}]$, $(K_{0.70}Ba_{0.29}Sr_{0.01})(K_{0.76}Na_{0.10}Ca_{0.03}Zr_{0.14})Na_{1.00}(Ti_{1.50}Nb_{0.22}Fe^{3+}{}_{0.12}Mg_{0.13})(O_{1.47}OH_{0.53})$ $[(Si_{3.95}Al_{0.04})O_{12}]$	*Ima*2	10.55	13.82	8.10				(3)
Batisite								
(1) $(Ba_{0.89}K_{0.11})(Na_{0.67}K_{0.22}Ca_{0.03}Zr_{0.09})Na_{1.00}(Ti_{1.70}Nb_{0.02}Mn_{0.01}Fe^{3+}{}_{0.14}Al_{0.11})(O_{1.88}OH_{0.12})[Si_4O_{12}]$		10.41	13.85	8.06				(3)
(2) $BaNa_2Ti_2O_2[Si_4O_{12}]$	*Ima*2	10.40	13.85	8.10				(4)
(3) $(Ba_{0.88}K_{0.12})_{1.00}(Na_{0.66}K_{0.22}Ca_{0.03}Sr_{0.02})Na_{1.00}(Ti_{1.68}Fe_{0.14}Zr_{0.09}Al_{0.11})(O_{1.66}(OH)_{0.34})[Si_4O_{12}]$		10.41(5)	13.85(5)	8.06(2)				(5)
$BaKNaTi_2O_2[Si_4O_{12}]$ “noonkanbahite”								
(1) $(Ba_{0.6}K_{0.4})(K_{0.7}Na_{0.3})Na(Ti_{0.72}Fe_{0.16}Nb_{0.06}Zr_{0.06})O_2[Si_4O_{12}]$	*Imam*	10.499(2)	13.913(4)	8.087(2)	2.997	2.940	2.695	(6)
(2) $(Ba_{0.55}K_{0.17}Ca_{0.18})K_{1.00}(Na_{0.81}K_{0.19})(Ti_{1.55}Fe_{0.18}Zr_{0.01}Al_{0.01}Si_{0.21})(O_{1.39}(OH)_{0.61})[Si_4O_{12}]$								(7)
(3) $(Ba_{0.73}Ca_{0.11}Na_{0.10})K_{1.00}Na_{1.00}(Ti_{1.46}Fe_{0.37}Mn_{0.02})(O,OH)_2[Si_4O_{12}]$	*Ima*2	10.505(9)	13.895(9)	8.142(6)	2.977	2.917	2.710	(8)

References: (1) This work, (2) Es'kova & Kazakova (1954), (3) Sokolova *et al.* (1964), (4) Nikitin & Belov (1962), (5) Kravchenko *et al.* (1960), (6) Schmahl & Tillmanns (1987), (7) Prider (1965), (8) Rastsvetaeva *et al.* (1997).

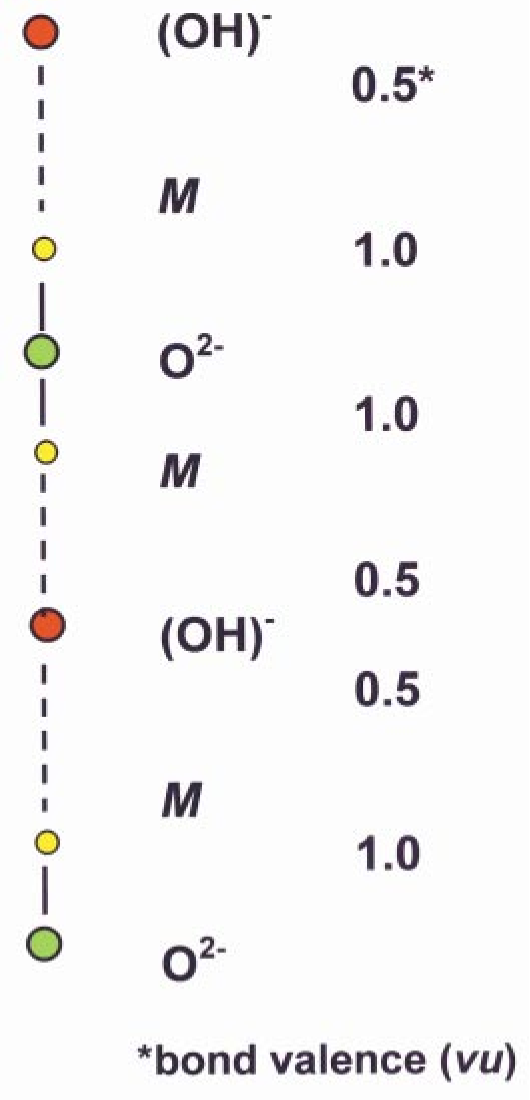

FIG. 4. Sketch of the ideal bond-valences associated with both O^{2-} and $(OH)^-$ occurring as bridging anions along a $[Ti^{4+}\phi_5]$ chain; Ti^{4+} cations are shown as yellow spheres, O^{2-} and $(OH)^-$ anions are shown as green and red circles, respectively.

Schmahl & Tillmanns (1987) reported the crystal structure of batisite with the chemical formula $(Ba_{0.6}\ K_{0.4})$ $(K_{0.7}\ Na_{0.3}])$ Na $(Ti^{4+}{}_{1.72}\ Fe^{3+}{}_{0.16}\ Nb_{0.06}\ Zr_{0.06})_2\ O_2$ $[Si_4O_{12}]$. This "batisite" actually corresponds to the "noonkanbahite" formula indicated above. Furthermore, Mitchell (1990) reported the occurrence of shcherbakovite in leucite phlogopite lamproites from the Leucite Hills, Wyoming, and Hogarth (1997) reported shcherbakovite–batisite from leucite phlogopite lamproite dykes from southeastern Baffin Island, Canada, but the compositions reported correspond to that of "noonkanbahite" given above. We currently have a proposal submitted to the Commission on New Minerals and Mineral Names of the International Mineralogical Association for approval of "noonkanbahite" as a new mineral species.

Ba, K or Nb may be absent in natural examples, whereas Na and Ti always occur in excess of 0.8 and 1.3 *apfu*, respectively (Schmahl & Tillmanns 1987, this work). The excess of Si above the ideal value of 4, which commonly occurs in natural batisite and shcherbakovite, possibly reflects the presence of small amounts of unaccounted OH^- groups (Es'kova & Kazakova 1954, Kravchenko *et al.* 1960, Prider 1965).

The principal substitutions by which additional cations are incorporated into this structure type are as follows:

$$Ba + Ti^{4+} \leftrightarrow (K,Na) + Nb$$

$$2Ti^{4+} \leftrightarrow Fe^{3+} + Nb$$

Schmahl & Tillmanns (1987) gave the general formula of the shcherbakovite–batisite minerals as $A_3\ M_2\ O_2$ $[Si_4O_{12}]$. On the basis of the structure of these minerals, it is more appropriate to write the formula as $A\ B\ C\ M_2$ $\phi_2\ [Si_4O_{12}]$, where A = Ba, K, Na, Ca; B = K, Na; C = Na, Ca; M = Ti^{4+}, Nb, Fe^{3+}, Zr; ϕ = O, (OH).

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